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Catalysis Today 132 (2008) 93–100
CATALYSIS TODAY
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A new low-temperature methanol synthesis method: Mechanistic and kinetics study of catalytic process

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Abstract

Mechanism and kinetics of catalytic process for a new low-temperature methanol synthesis on Cu/ZnO catalysts from syngas ($CO/CO_2/H_2$) using catalytically active alcohol promoters were investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Two intermediate species, adsorbed formate species and alkyl formate species, were formed in this synthesis process. The adsorbed formate species easily reacted with ethanol or 2-propanol at 443 K and atmospheric pressure, and the reaction rate with 2-propanol was faster than that with ethanol. Alkyl formate was readily reduced to form methanol at 443 K and 1.0 MPa, and the hydrogenation rate of 2-propyl formate was found to be quicker than that of ethyl formate. As a promoter, 2-propanol exhibited a higher activity than ethanol in the reaction of the low-temperature methanol synthesis.

Keywords: In situ DRIFT; Methanol; Ethanol; 2-Propanol; Formate; Cu/ZnO; Syngas ($CO/CO_2/H_2$)

1. Introduction

Methanol is a basic chemical, a kind of transportation fuel and energetic material for fuel cells, being produced at 30–40 million tonnes per year around the world, from carbon monoxide and hydrogen (syngas) where several percent of carbon dioxide is included. It is now commercially produced by ICI process under high temperature and high pressure (523–573 K, 5–10 MPa), using copper–zinc-based oxide catalyst. However, the efficiency of methanol synthesis is severely limited by thermodynamics because methanol synthesis is an extremely exothermic reaction [1,2]. For example, at 573 K and 5 MPa, the theoretical maximum of one-pass CO conversion is around 20%. As a means to reduce the production costs and utilize the thermodynamic merit of this reaction, low-temperature synthesis of methanol is challenging and important [3].

BNL method developed by Brookhaven National Laboratory of USA realized this synthesis at 373–403 K and 1.0–5.0 MPa, using very strong base catalyst (mixture of NaH, alcohol and acetate) and pure syngas ($CO + H_2$). However, a remarkable drawback of this process is that trace amount of carbon dioxide and water in the feed gas or reaction system will deactivate the strongly basic catalyst soon [4,5], which implies high cost from the complete purification of the syngas made from the methane reformer, coal or biomass gasification, as well as the reactivation process of the deactivated catalyst.

Methanol synthesis from pure CO and H_2 via the formation of methyl formate has been widely studied, where carbonylation of methanol and hydrogenation of methyl formate were considered as two main steps of the reaction [6,7].

$$CO + CH_3OH \overset{\text{RONa}}{=} HCOOCH_3 \quad (1)$$

$$HCOOCH_3 + 2H_2 \overset{\text{Solid Cat.}}{=} 2CH_3OH \quad (2)$$

$$CO + 2H_2 = CH_3OH \quad (3)$$

Similar to the BNL method, in this process, CO_2 and H_2O act as poisons to the alkoxide catalyst (RONa) and must be

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doi:10.1016/j.cattod.2007.12.002

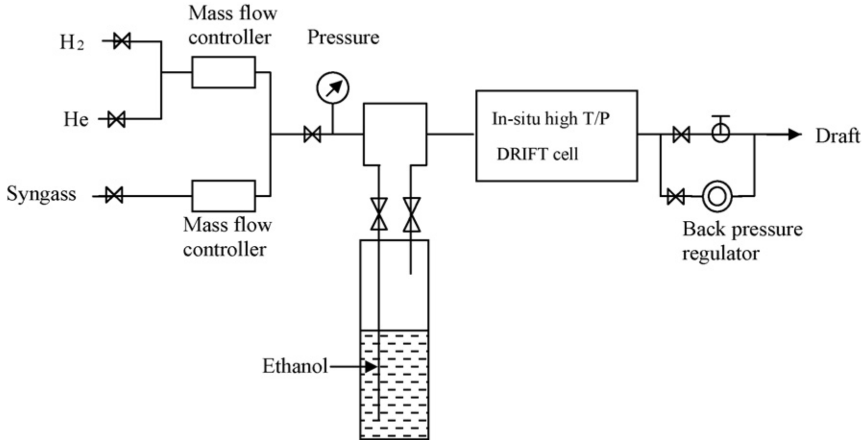


Fig. 1. The scheme of in situ DRIFT apparatus for adsorption and reaction.

completely removed from syngas, making commercialization of low-temperature methanol synthesis impossible now.

The present authors reported that alcohol solvent, as well as Cu/ZnO catalyst remarkably lowered the reaction temperature of methanol synthesis from syngas containing carbon dioxide, by which methanol was produced at 443 K and 3.0 MPa [8–10]. Furthermore, as alcohol solvent contained small amount of water in this study, it is considered that this new process can use low-grade syngas containing carbon dioxide and water without purification. As expected, low-reaction temperature realized high CO conversion as 50–80% [10–13].

Until now, many different views have been proposed regarding the nature of the adsorbed intermediate species on catalysts for high-temperature methanol synthesis reaction [14–17]. Most of the experimental data supporting these views were based on the FTIR spectroscopy of the adsorbed species formed during the reaction of hydrogenation of CO and/or CO_2. Many studies showed that the nature of the adsorbed intermediate species on catalysts for methanol synthesis reaction depended on the component of catalyst system and the preparation condition of the catalysts [18–22]. Although many studies focused on reaction mechanism of methanol synthesis on Cu/ZnO catalysts, the methanol synthesis at low temperature from $CO/CO_2/H_2$ on Cu/ZnO using catalytically active alcohol promoter is a new process proposed by the present authors, and its mechanism is not clear until now. In the present work, the nature of intermediate species and the reaction kinetic for low-temperature methanol synthesis above is investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The promoting action of catalytically active alcohol involved in the reaction is discussed.

2. Experimental

The catalyst was prepared by co-precipitation method. An aqueous solution containing copper, zinc nitrates (Cu/Zn in molar ratio = 1) and an aqueous solution of sodium carbonate were added simultaneously to water of 300 ml with constant stirring. The precipitation temperature and pH value were maintained at 333 K and 8.5, respectively. The obtained precipitate was filtrated and washed with distilled water, followed by drying at 393 K for 6 h and calcination in air at 623 K for 1 h. This precursor was then reduced by a flow of 5% hydrogen in nitrogen at 493 K for 10 h and successively passivated by 1% oxygen diluted by nitrogen.

In situ DRIFT spectra were collected on a Nicolet Nexus 470 FT-IR spectrometer supplied with a diffuse reflectance attachment and with a MCT detector. The catalyst powder weighing approximately 14 mg was contained in a diffuse reflectance infrared cell with a ZnSe window which can work at high temperature and high pressure. In situ absorbance spectra were obtained by collecting 32 scans at 2 cm^{-1} resolution. Each spectrum was then referenced to a spectrum of the catalyst collected at the same temperature under He or H_2 flow as appropriate. The apparatus scheme is shown in Fig. 1. Syngas used in this experiment was $CO/CO_2/H_2/Ar$ at a ratio of 32/5/61/2, the same composition to those used in catalyst development [9–13].

Before the adsorption of reactant, the catalyst sample was treated in situ in He stream flowing at 20 $cm^3 min^{-1}$ at 298 K for 20 min, and then 493 K for 20 min. The catalyst sample was reduced in H_2 stream flowing at 20 $cm^3 min^{-1}$ at 493 K for 1 h, and then in He at 493 K for 1 h. Subsequently the catalyst sample was cooled down in He to the adsorption temperature.

3. Results and discussion

3.1. Formation and hydrogenation reaction of the formate species

The catalyst was exposed to $CO/CO_2/H_2/Ar$ at 443 K and atmospheric pressure for 10 min followed by hydrogen flowing at a total rate of 20 $cm^3 min^{-1}$ at 443 K for 30 min. The formation and hydrogenation spectra of the formate species on Cu/ZnO are shown in Fig. 2a and b. Assignment of the bands for adsorption species was made by analogy with the spectra of known compounds and by comparison with published literatures. The bands at 2966, 2873, 1572, 1370, 1362 cm^{-1} can be attributed to bidentate formate species on ZnO

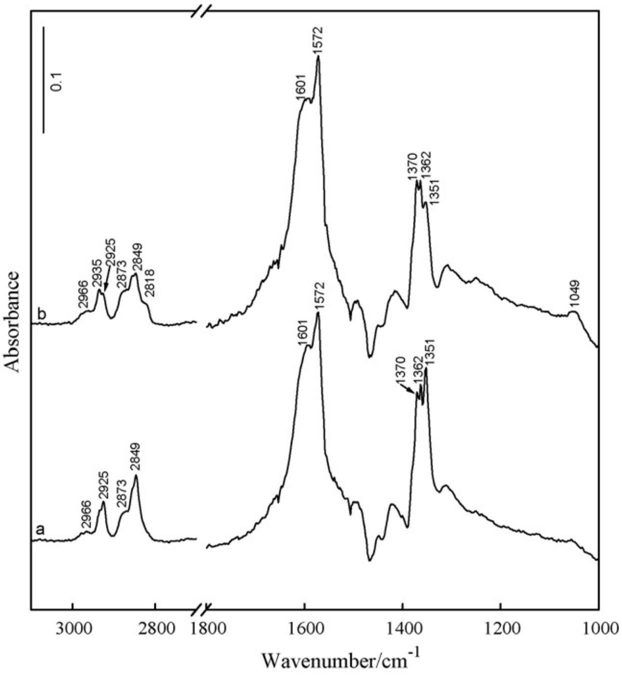


Fig. 2. In situ DRIFT spectra of formation and hydrogenation of formate species at 443 K and atmospheric pressure on Cu/ZnO: (a) formate adsorption species and (b) after reaction with H_2 for 30 min.

(b-HCOO-Zn), at 2925, 2849, 1351 cm^{-1} can be attributed to bidentate formate species on Cu (b-HCOO-Cu), which are stretching vibration of the carbon–hydrogen bond (νCH, 2966, 2873, 2925 and 2849 cm^{-1}), antisymmetric and symmetric stretching vibration of carbon–oxygen band (ν_{as}OCO 1572 and ν_sOCO 1370, 1362, 1351 cm^{-1}), respectively [14–16,22–27]. HCOO-Zn may be produced by CO reacting with hydroxyl on Zn, or by CO_2 reacting with hydroxyl to form carbonate, and then carbonate is reduced by hydrogen [25]. The presence of b-HCOO-Cu may be the result of CO_2 reacting with hydrogen on the Cu [16]. Fig. 2a sufficiently shows that during syngas containing CO_2 adsorption on Cu/ZnO, a formate entity is formed and that this species appears as one of the possible intermediate of the conventional, high-temperature methanol synthesis. This experiment result is the same to those in several previous studies [14–16,22–25].

The bands intensity of b-HCOO-Zn (2966, 2873, 1572, 1370, 1362 cm^{-1}) does not change clearly, and the bands intensity of b-HCOO-Cu (2925, 2849, 1351 cm^{-1}) is decreased slightly after hydrogenation reaction for 30 min at 443 K in Fig. 2b. The weak bands at 2935, 2818 cm^{-1} (νCH) and 1049 cm^{-1} (νC–O) can be attributed to the methoxy groups [28,29], and its bands intensity increases slightly after reaction in Fig. 2b. These results prove that the hydrogenation reaction of formate species is difficult at temperature as low as 443 K and atmospheric pressure, although formate species can be formed easily on Cu/ZnO catalyst at low temperature. It implies that the hydrogenation reaction activity of HCOO-Cu is higher than HCOO-Zn [25], and the formation of small amount of methoxy species is due to hydrogenation reaction of HCOOCu at 443 K and atmospheric pressure. The band at 1601 cm^{-1} is H_2O on Cu in Fig. 2 [16].

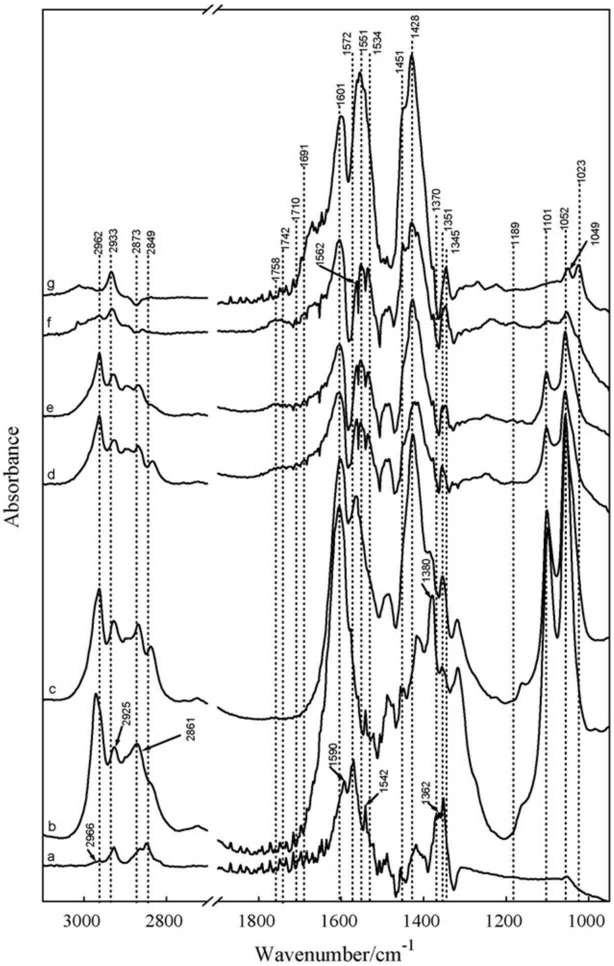


Fig. 3. In situ DRIFT spectra of the reaction for adsorbed formate with ethanol between 298 and 443 K at atmospheric pressure in He: (a) formate adsorption species, reacting with ethanol at (b) 298 K, (c) 343 K, (d) 373 K, (e) 393 K and (f) 443 K, respectively; (g) sweeping in He for 20 min at 443 K.

3.2. Reaction of the adsorbed formate with ethanol

Fig. 3 shows the spectra of reaction for adsorbed formate with ethanol between 298 and 443 K at atmospheric pressure. The saturating ethanol vapor (298 K) was carried by helium into an IR cell at 298 K for 2 min after formation of formate species on Cu/ZnO, then closing the IR cell with the vapor in. Spectra of the reaction were obtained after 30 min at each temperature and at last swept in helium at 443 K for 20 min. The band intensities of formate adsorption species are decreased with temperature increase, and these bands disappear when the temperature is higher than 393 K. The disappearance of formate absorption bands at 2849, 1370, 1362, and 1351 cm^{-1}, which are not interfered by the bands of adsorbed ethoxy and other species, can be observed clearly, but we cannot determine the change of other formate absorption bands due to interfering action of ethoxy and other by-product absorption bands. The bands of gas-phase ethyl formate (1758, 1742, 1189 cm^{-1}) and physisorbed ethyl formate (1710, 1691 cm^{-1}) can be detected when the temperature rises to 373 K. The bands at wavenumbers of 2962, 2925, 2861, 1380, 1101, and 1052 cm^{-1} can be attributed to the ethoxy adsorbed on Cu/ZnO, those at 2933, 1562, 1451, 1049, and 1023 cm^{-1} to

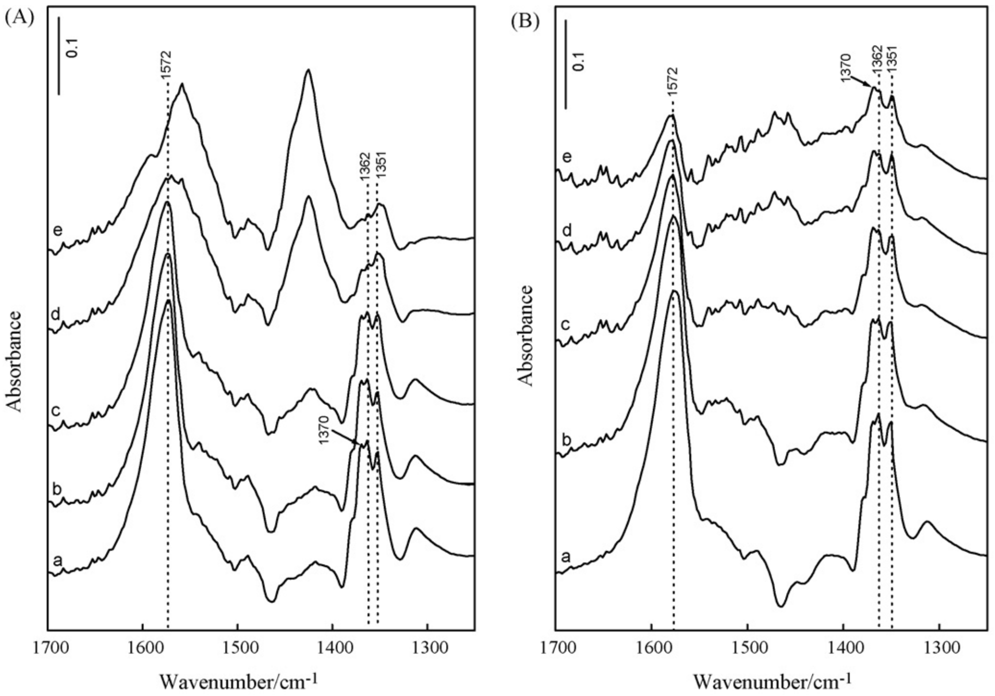


Fig. 4. In situ DRIFT spectra of the reaction for adsorbed formate with ethanol (A) and 2-propanol (B) at 443 K and atmospheric pressure in He: (a) formate adsorption species, subsequent reaction with ethanol after (b) 0.5 min, (c) 1 min, (d) 2 min and (e) 3 min.

acetate species adsorbed, and those at 1551, 1534, 1345, and 1428 cm^{-1} to carbonate species [16,22,29,30]. The band intensity of ethoxy adsorption species decreases with temperature increase. This may be due to the carbonate adsorption species and acetate adsorption species to be formed by dehydrogenation of the ethoxy group. To confirm the assignment of ethoxy species and its transforming action, experiments of ethanol or acetic acid adsorption were conducted on Cu/ZnO between 298 and 443 K. The acetate and carbonate species are derived from ethoxy dehydrogenation with temperature increase [29,30].

Although the hydrogenation reaction of formate adsorption species is difficult at 443 K and atmospheric pressure, the experimental results in Fig. 3 show that the band intensity of the formate adsorption species decreases progressively, and at last these species disappear with temperature increase from 298 to 443 K when ethanol is introduced into the reaction system at atmospheric pressure. This indicates that the formate adsorption species can react easily with ethanol at low temperatures and atmospheric pressure. It implies that the reaction of formate species can be accelerated by ethanol introduced into reaction system.

On the other hand, as previously reported [28], 2-propanol used in this reaction not only significantly decreased the reaction temperature due to its promotional action, but also was not consumed due to its regeneration by hydrogenation of the 2-propyl formate, acting like a catalytic solvent.

3.3. Influence of different alcohol on reaction activity

Saturating ethanol vapor (7.9 kPa) was introduced into IR cell with helium at 443 K and atmospheric pressure after formation of formate species on Cu/ZnO, the spectra were obtained after reaction at 443 K for 0.5, 1, 2, and 3 min, respectively in Fig. 4A. In another experiment, saturating 2-propanol vapor (7.9 kPa) was carried by helium into IR cell at 443 K and atmospheric pressure after formation of formate species on Cu/ZnO, the spectra were obtained after reaction at 443 K for 0.5, 1, 1.5 and 2 min, respectively in Fig. 4B. The results show that the band intensity of formate species (1572, 1370, 1362, 1351 cm^{-1}) decreases with increasing reaction time in Figs. 5 and 6. In order to compare the reaction activity using different alcohols, the reaction kinetic analysis is necessary for the reactions in Fig. 4A and B. It is notable that there are two types of formate species in reaction system, HCOOCu and HCOOZn species. The reaction kinetic analysis of the formate species was represented by the reaction of HCOOCu or HCOOZn with alcohol.

The reactions of formate species obey a first-order reaction kinetic model because the dosage of alcohol is constant in the flowing reaction system. Therefore, the reaction rate of formate species with alcohol should be expressed as below:

$$r_{(\mathrm{HCOOCu})} = k_1 C_{(\mathrm{HCOOCu})}, \qquad r_{(\mathrm{HCOOZn})} = k_2 C_{(\mathrm{HCOOZn})}$$

where k_1 and k_2 are the rate constants, and $C_{(\mathrm{HCOOCu})}$ and $C_{(\mathrm{HCOOZn})}$ are the concentrations of HCOOCu and HCOOZn species on catalyst surface, which is in direct proportion to the peak area of HCOOCu, HCOOZn species. Fig. 5A and B shows that the variation of $\ln(C_0/C)$ as a function of t (min) in the reaction process, where C_0/C corresponds to A_0/A. A_0 is initial peak area of HCOOCu or HCOOZn species, A is peak area at t min. The peak areas of HCOOCu species at 1351 cm^{-1} and HCOOZn species at 1362 cm^{-1} were calculated with reaction

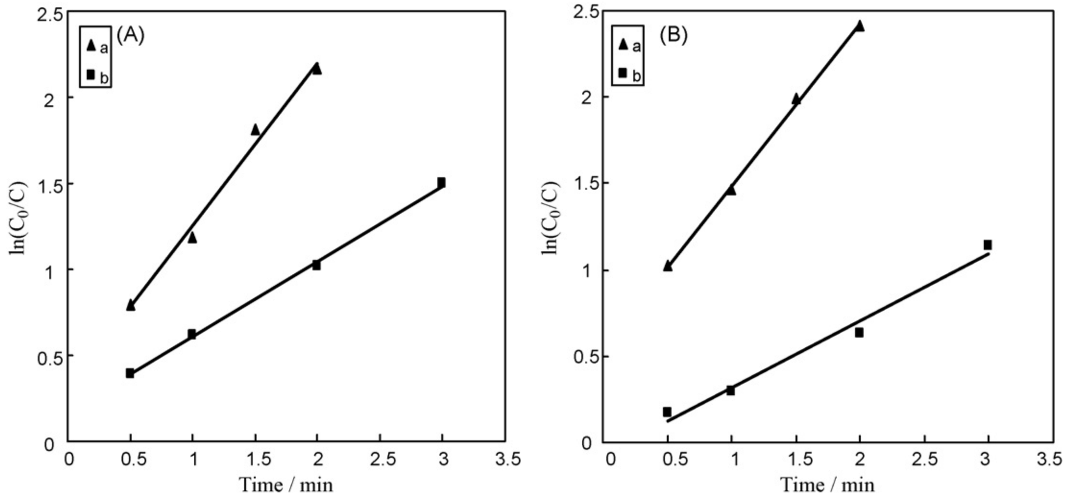
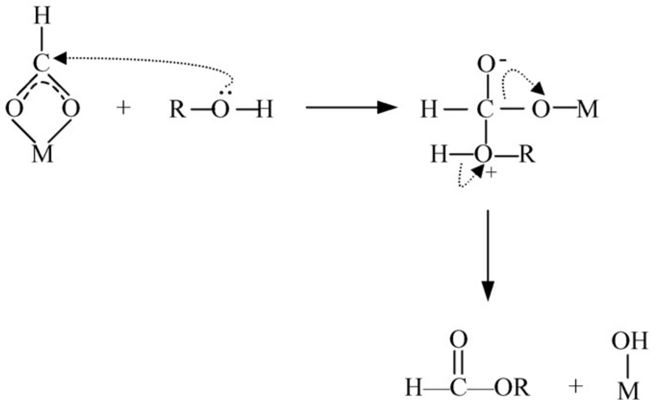


Fig. 5. The variation of $\ln(C_0/C)$ as a function of t (min) in the reaction process of HCOOCu (A) and HCOOZn (B) species with alcohol (a) 2-propanol and (b) ethanol.

proceeding in Fig. 4A and B. Fig. 5A indicates that the reaction rate constant of HCOOCu species with ethanol is 0.4381 min^{-1}, and with 2-propanol is 0.9463 min^{-1}, and Fig. 5B indicates that the reaction rate constant of HCOOZn species with ethanol is 0.3845 min^{-1}, and with 2-propanol is 0.9370 min^{-1}. The reaction rate constant of HCOOCu or HCOOZn species with 2-propanol is larger than that with ethanol. Therefore, it can be concluded that the reaction rate of formate adsorption species with 2-propanol is faster than that of them with ethanol.

This reaction is a nucleophilic addition–elimination reaction, and alcohol is the nucleophilic reagent of the reaction. The reaction route is represented as follows:



[M is Cu or ZnO, R is C_2H_5 or $(CH_3)_2CH$]

2-Propanol has higher electron density on its oxygen atom than ethanol due to its larger electron-releasing inductive effect from two methyl groups, although spatial obstacle of 2-propanol is slightly larger in the nucleophilic attack, as a balanced effect between electronic factor and spatial factor, 2-propanol exhibited the higher activity.

3.4. Hydrogenation of alkyl formate

In order to prove the hydrogenation reaction of alkyl formate to produce methanol, the Cu/ZnO catalysts were exposed to the inlet partial pressure 28.5 kPa of ethyl formate or 2-propyl formate using hydrogen to balance the total pressure to 1.0 MPa at 298 K, and then closing IR cell with 1.0 MPa reactants inside and increasing temperature to 443 K. The hydrogenation spectra of ethyl formate were collected at regular intervals in 1 h at 443 K and 1.0 MPa in Fig. 6A. The hydrogenation spectra of 2-propyl formate were collected at regular intervals in 1 h at 443 K and 1.0 MPa in Fig. 6B. The results indicate that the band intensity of gas-phase ethyl formate (1758, 1753, 1742, 1189 cm^{-1}) or the band intensity of gas-phase 2-propyl formate (1753, 1743, 1739, 1190 cm^{-1}) decreases with increasing reaction time, and at last these bands disappear, while the bands of gas-phase methanol species (1056, 1032, 1008 cm^{-1}) are clearly observed with increasing time of the hydrogenation reaction at 443 K and 1.0 MPa in Fig. 6A or B. The bands of gas-phase ethanol (1065, 1056 cm^{-1}) are observed in Fig. 6A, while the bands of gas-phase 2-propanol (1147 cm^{-1}) are also observed in Fig. 6B. These results indicate that gas-phase ethyl formate or 2-propyl formate is reduced easily by hydrogen atoms on Cu to form methanol at temperature as low as 443 K and 1.0 MPa. In fact, ethyl formate or 2-propyl formate is also reduced easily to form methanol at low temperature and atmospheric pressure (this experiment is not shown here). However, in order to observe clearly the bands of gas-phase methanol and to conduct the kinetic analysis below, the hydrogenation reaction of alkyl formate is accelerated under increased pressure of hydrogen and the vapor pressure of alkyl formate here. It is notable that the hydrogenation reaction rate of physisorbed alkyl formate is very rapid even at 373 K and atmospheric pressure (this experiment is not shown here), and this physisorbed species is not observed at 443 K, because its hydrogenation reaction was finished in the process of rapidly increasing temperature from 298 to 443 K at 1.0 MPa in this study.

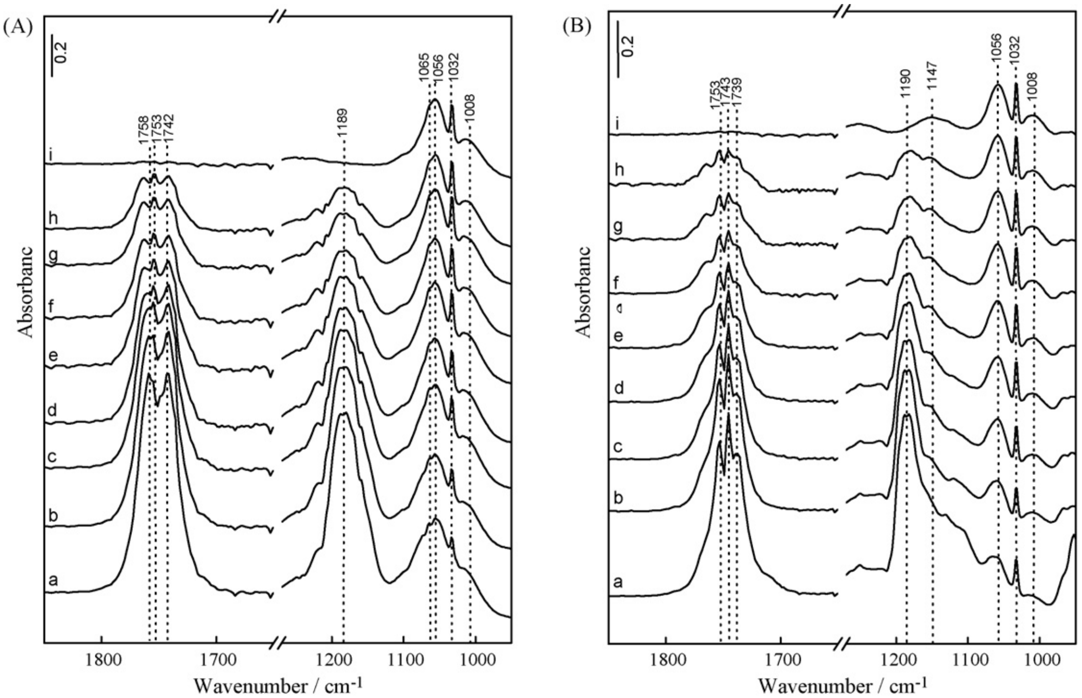


Fig. 6. In situ DRIFT spectra of the hydrogenation reaction of ethyl formate (A) and 2-propyl formate (B) on Cu/ZnO at 443 K and 1.0 MPa: (a) 0 min, (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min, (f) 4 min, (g) 5.5 min, (h) 7 min and (i) 1 h.

In order to compare the hydrogenation reaction activity of different alkyl formates, the reaction kinetic analysis is conducted for the reaction in Fig. 6A and B. The hydrogenation reactions for alkyl formate obey first-order reaction kinetic model because high-pressure hydrogen is excessive in the reaction process. Therefore, the hydrogenation reaction rate of alkyl formate is expressed as below:

$$r_{(\mathrm{HCOOR})} = k_3 P_{(\mathrm{HCOOR})}$$

where k_3 is the rate constant and $P_{(\mathrm{HCOOR})}$ is the partial pressure of gas-phase alkyl formate species, which is in direct proportion to the peak area of gas-phase alkyl formate species. Fig. 7 shows that the variation of $\ln(P_0/P)$ as a function of t (min) in the reaction process, where P_0/P corresponds to A_0/A. A_0 is initial peak area of gas-phase alkyl formate species, A is peak area at t min. The peak areas of gas-phase alkyl formate (ethyl formate peaks at 1758, 1753, 1742 cm^{-1}, 2-propyl formate peaks at 1753, 1743, 1739 cm^{-1}) were calculated with reaction

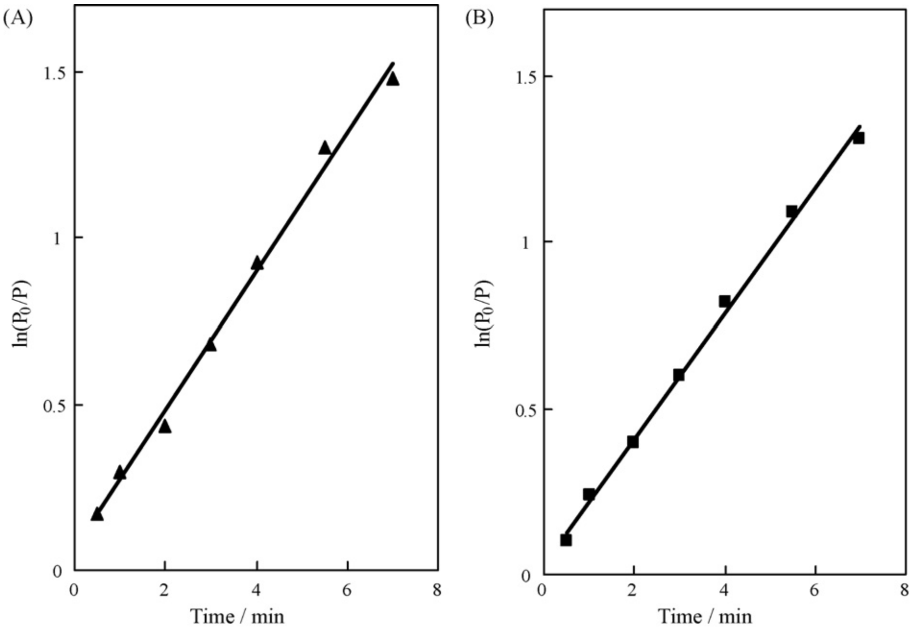


Fig. 7. The variation of $\ln(P_0/P)$ as a function of t (min) in the hydrogenation reaction process of alkyl formate species (A) 2-propyl formate and (B) ethyl formate.

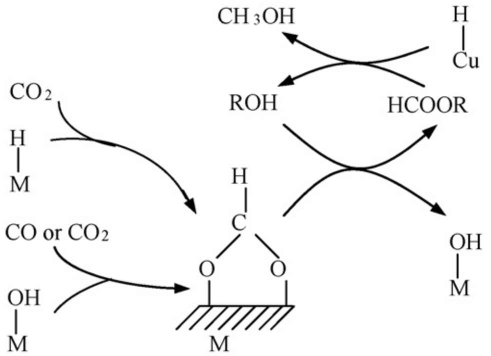


Fig. 8. Proposed mechanism for the synthesis reaction of low-temperature methanol from syngas ($CO/CO_2/H_2$) using alcohol promoter [M is Cu/ZnO, R is C_2H_5 or $(CH_3)_2CH$].

proceeding in Fig. 6A and B. Fig. 7 indicates that the hydrogenation reaction rate constant of ethyl formate is 0.1878 min^{-1}, and the reaction rate constant of 2-propyl formate is 0.2084 min^{-1}. Therefore, the hydrogenation reaction rate of 2-propyl formate is faster than that of ethyl formate.

Based on the observation above, a possible mechanism is offered as scheme in Fig. 8 for methanol synthesis at low temperature from syngas ($CO/CO_2/H_2$) using alcohol promoter on Cu/ZnO catalyst. In this scheme, at first the formate adsorption species are produced by exposing syngas ($CO/CO_2/H_2$) to Cu/ZnO catalyst surface, and then the nucleophilic addition–elimination reaction of the formate adsorption species with alcohol proceeds on Cu/ZnO catalyst surface to form the gas-phase and physisorbed alkyl formate, at last the alkyl formate is reduced by hydrogen atoms on Cu to form gas-phase methanol. The experiment results above prove that the adsorbed formate species, an intermediate in conventional, high-temperature methanol synthesis reaction, are hardly reduced to form methanol on Cu/ZnO catalyst at 443 K and atmospheric pressure. Therefore, the conventional methanol synthesis reaction must proceed at high temperature and high pressure, using copper–zinc-based oxide catalyst [1–3]. However, our experiments prove that it is very easy for the adsorbed formate species to react with alcohol, such as, ethanol or 2-propanol, to produce alkyl formate on Cu/ZnO catalyst at 443 K and atmospheric pressure, and alkyl formate is also reduced easily to form methanol at 443 K.

The formation of alkyl formate is a key step in low-temperature methanol synthesis. The alcohol introduced into the reaction system altered the normal reaction path of the conventional, high-temperature methanol synthesis, which was from formate via methoxy to methanol, a high-temperature step. The reaction of low-temperature methanol synthesis on Cu/ZnO proceeded through a new path, which was from formate via alkyl formate to methanol. The alcohol used in this reaction not only significantly decreased the reaction temperature due to its promoting action, but also was not consumed due to its self-regeneration by hydrogenation of alkyl formate, acting like a catalytic solvent.

Kinetic analysis results indicate that the reaction rate of 2-propanol with formate species is faster than that of ethanol, while the hydrogenation reaction rate of 2-propyl formate is also faster than that of ethyl formate. Therefore, although the reaction of methanol synthesis is promoted by either ethanol or 2-propanol, the promoting effects of 2-propanol are bigger than that of ethanol. In fact, the present authors have proved that the reaction activity of low-temperature methanol synthesis is different when alcohols with different structure are used as promoter [10,12], and the yield of methanol and total carbon conversion are higher for 2-propanol as promoter than ethanol in the actual reaction of low-temperature methanol synthesis [12].

4. Conclusions

In situ DRIFTS was used to study the spectroscopy and kinetics of catalytic process for a new low-temperature methanol synthesis method on Cu/ZnO catalyst from $CO/CO_2/H_2$ using alcohol promoter. The results show that two types of intermediate species, formate adsorption species and alkyl formate species, were produced in this synthesis process. The adsorbed formate species were formed by exposing Cu/ZnO catalyst to $CO/CO_2/H_2$, while gas phase and physisorbed alkyl formate were formed by the nucleophilic addition–elimination reaction of adsorbed formate species with alcohol at 443 K, and then alkyl formate was reduced by hydrogen atoms on Cu to form methanol at 443 K. The reaction temperature was significantly decreased due to the promotional catalytically active action of alcohol and a new reaction route, as alcohol used in this reaction was not consumed due to its self-regeneration by hydrogenation of alkyl formate, acting like a catalytic solvent. Kinetic analysis shows that the low-temperature methanol synthesis reaction was faster by using 2-propanol as promoter than using ethanol on Cu/ZnO catalyst at 443 K, in good accordance to the catalytic reaction results.

It is a key step for the reaction of formate adsorption species with alcohol to form alkyl formate intermediate at temperature as low as 443 K. It changed the normal reaction path of conventional, high-temperature methanol synthesis, which was from formate via methoxy to methanol. Low-temperature methanol synthesis reaction proceeded through a new route, which was from formate via alkyl formate to methanol.

References

[1] R.G. Herman, G.W. Simmons, K. Klier, Stud. Surf. Sci. Catal. 7 (1981) 474.
[2] G.H. Graaf, P. Sijtsema, E.J. Stamhuis, G. Oostem, Chem. Eng. Sci. 41 (1986) 2883.
[3] M. Marchionna, M. Lami, A. Galleti, Chemtech 27 (1997) 27.
[4] J. Haggin, Chem. News Eng. 21 (1986), August 4.
[5] Brookhaven National Laboratory, US Patents 461,479, 4,619,946, 4,623,634, 4,613,623 (1986), 4,935,395 (1990).
[6] V.M. Palekar, H. Jung, J.W. Tierney, I. Wender, Appl. Catal. A 102 (1993) 13.
[7] K. Othmer, second ed., Encyclopedia of Chemical Technology, vol. 13, Wiley, New York, 1964, p. 390.
[8] N. Tsubaki, Y. Sakaiya, K. Fujimoto, Appl. Catal. A 180 (1999) L11.
[9] N. Tsubaki, M. Ito, K. Fujimoto, J. Catal. 197 (2001) 224.

[10] N. Tsubaki, J.Q. Zeng, Y. Yoneyama, K. Fujimoto, Catal. Commun. 2 (2001) 213.

[11] R. Yang, Y. Fu, Y. Zhang, N. Tsubaki, J. Catal. 228 (2004) 23.

[12] J.Q. Zeng, K. Fujimoto, N. Tsubaki, Energy Fuels 16 (2002) 83.

[13] R. Prasert, T. Yamagami, V. Tharapong, Y. Yoneyama, M. Ito, N. Tsubaki, Energy Fuels 17 (2003) 817.

[14] I.A. Fisher, A.T. Bell, J. Catal. 178 (1998) 153.

[15] J.F. Edwards, G.L. Schrader, J. Catal. 94 (1985) 175.

[16] I.A. Fisher, A.T. Bell, J. Catal. 172 (1997) 222.

[17] X. Mugniery, T. Chafik, M. Primet, D. Bianchi, Catal. Today 52 (1999) 15.

[18] N.Y. Topsøe, H. Topsøe, J. Mol. Catal. A 141 (1999) 95.

[19] J. Greeley, A.A. Gokhale, J. Kreuser, J.A. Dumesic, H. Topsøe, N.Y. Topsøe, M. Mavrikakis, J. Catal. 213 (2003) 63.

[20] T. Fujitani, J. Nakamura, Appl. Catal. A 191 (2000) 111.

[21] S. Fujita, S. Moribe, Y. Kanamori, M. Kakudate, N. Takezawa, Appl. Catal. A 207 (2001) 121.

[22] D. Bianchi, T. Chafik, M. Khalfallah, S.J. Teichner, Appl. Catal. A 105 (1993) 223.

[23] D.L. Roberts, G.L. Griffin, J. Catal. 101 (1986) 201.

[24] S. Takafumi, Y. Iwasawa, J. Catal. 129 (1991) 343.

[25] S. Fujita, M. Usui, H. Ito, N. Takezawa, J. Catal. 157 (1995) 403.

[26] G.J. Millar, C.H. Rochester, K.C. Waugh, J. Chem. Soc., Faraday Trans. 88 (1992) 3497.

[27] G.J. Millar, C.H. Rochester, K.C. Waugh, J. Chem. Soc., Faraday Trans. 87 (1991) 2785.

[28] R. Yang, Y. Zhang, N. Tsubaki, Catal. Commun. 6 (2005) 275.

[29] A. Yee, S.J. Morrison, H. Idriss, J. Catal. 186 (1999) 279.

[30] A. Yee, S.J. Morrison, H. Idriss, J. Catal. 191 (2000) 30.